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Mass spectrometry	Chemical ionization	Dimethyl sulfoxide
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

An analytical technique called Ionic Cluster Mass Spectrometry (ICMS) has been developed. The technique is akin to chemical ionization mass spectrometry in that both concepts rely upon the mass analysis of ions that are products of ion-molecule reactions occurring in a reactant gas in the ion source. ICMS employs moist air as the reactant gas at ion source pressures of 10 mmHg to 1 atmosphere. Samples can be injected directly into the ion source in a clean, moist airstream or ambient atmosphere may constitute the reactant gas plus sample.

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20. ABSTRACT (Continued)

ICMS analyses of organic vapors in air have been used to aid in the establishment of response mechanisms in the Ionization Detector System (IDS). Ionic clusters to which the IDS respond have been identified. The conclusion drawn from these studies is that differential diffusion of ionic clusters from an airstream predominates in the physics of the response mechanism.

PREFACE

This work was authorized under Project/Task 1W762710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The work covered by this report began in June 1972 and terminated in April 1974.

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Acknowledgment

The authors acknowledge the technical efforts of J. A. Parsons and D. J. Buckley who gathered most of the experimental data.

3

CONTENTS

LIST OF FIGURES

IONIC CLUSTER MASS SPECTROMETRY. I. DETECTION AND IDENTIFICATION OF AIRBORNE ORGANIC VAPORS AND ESTABLISHMENT OF OPERATIONAL MECHANISMS IN THE IONIZATION DETECTOR SYSTEM

I. INTRODUCTION.

The study of proton ion/dipole clusters in the gas phase[1-4] has been extended in connection with the search for new concepts in chemical agent (and other atmospheric contaminants) detection. The result has been an analytical technique called Ionic Cluster Mass Spectrometry (ICMS).[5] ICMS is akin to the technique of chemical ionization (CI) mass spectrometry in that both concepts rely upon the mass analysis of ions that are products of ion-molecule reactions occurring in a reactant gas in the ion source. At atmospheric pressure in the ion source the technique has been termed Atmospheric Pressure Ionization (API) Mass Spectrometry.[6] Users of API must take care to insure that the ion source is as free as possible of water vapor which will interfere with the ionization of the ultratrace amounts of samples to be analyzed. ICMS employs moist air as the reactant gas at ion source pressures of 10 mmHg to 1 atmosphere. The sample may be introduced into a clean, moist airstream or the sample plus reactant gas may constitute ambient atmosphere. Sample/reactant gas ratios may be as low as 5 mole parts in 10^{10}.

During the study to date of ICMS no fragmentation of sample molecules has been observed, only increases in sample mass by protonation and hydration. Since only cluster ions are observed the term ICMS is more descriptive of this mass-spectrometric-analysis technique.

Mechanisms, rate constants, and enthalpies of formation for ion clusters $H^+(H_2O)_n$ (derived from ion molecule reactions initiated by the primary ions N_2^+ and O_2^+) have been established where the primary ionization source has been electron irradiation,[7,8] in flowing afterglow experiments,[9] and in corona discharges.[5,10,11] For the ICMS technique, the hydrated proton species serve as precursors for clusters $H^+(H_2O)_n(A)_m$ which represent the qualitative and quantitative indicators of the trace compound A. The mechanism of formation of $H^+(H_2O)_n(A)_m$ is not dependent upon the method of formation of primary ions, i.e. electron impact (EI) or electrical discharges. The sensitivity of the technique is, however, dependent upon the *rate* of formation of the primary ions, the water vapor concentration, and the pressure of the reactant gas. A corona discharge was selected for most of this work because it is an extremely intense source of primary ions. A tritium β source proved to be a much more stable source of ions.

Some of the results of the ICMS studies have been applied to the establishment of the response mechanisms in the Ionization Detector System (IDS) now under development for the Army and the Air Force. The basic field unit, as it exists to date, has been developed by Minneapolis Honeywell, Inc. The mechanism by which the IDS selectively responds to chemical agents in the atmosphere has not been fully understood. The construction details, sensitivity, and specificity of the system have been given in a contractor report.[12]

II.   EXPERIMENTAL.

Figure 1 is a diagram of the ICMS apparatus. Ions produced in a corona discharge or as a result of ion-molecule reactions (formed at room temeprature, $\sim 25^\circ C$) diffuse through a pinhole into a vacuum chamber where they are focused into a quadrupole mass spectrometer. Ion detection is accomplished with an electron multiplier coupled to a high-speed picoammeter or electrometer amplifier.
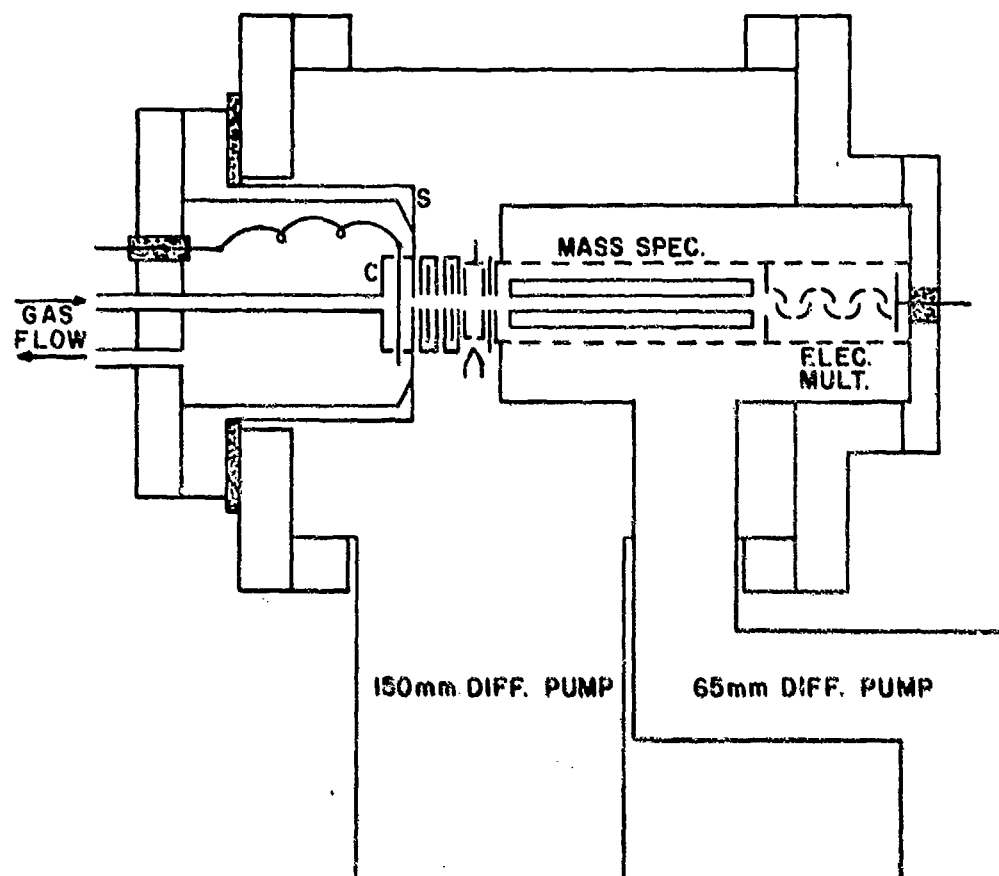
Figure 1. Schematic Diagram of the ICMS Apparatus

Air or nitrogen containing trace quantities of water vapor and the substance to be analyzed flow into the ion source — a corona discharge cylinder at C. The discharge is established between a 90% Pt — 10% Rh wire, 0.08-mm-diameter, and a stainless steel cylinder, 12-mm-ID, located coaxial to one another. The discharge current is maintained at 10 µa (for all source pressures) with a 6-kv variable power supply placed in series with a 4.7-megohm current-limiting resistor. Ions exit the source chamber by diffusion through an orifice, 35 microns in diameter, located in the center of S and are subsequently mass-analyzed.

Flow rate through the ion source is held constant for all pressures. Source pressures are varied to allow a control of the collision rate and the subsequent appearance and/or

8

disappearance of ionic species of interest. Analytical data is obtained when the source pressure is held constant and the sample concentration is variable.

A sketch of a detection cell in the IDS in the configuration used in this work is shown in figure 2. The system operates at atmospheric pressure. Air, heated to $60°C$ (the normal operating temperature of the IDS), is pumped through the cell at any desired flow rate. The cell is placed in a small oven so that $60°C$ is maintained throughout the cell. The airstream passes over a 1-Curie β-source (titanium tritide coated foil). The primary ions, N_2^+, O_2^+, and O_2^-, are formed near the β-source by electron impact or electron attachment. A sequence of ion-molecule reactions follows and equilibrium among ionic clusters is rapidly established. The mixture of air and ions then flows through a series of baffles to a Faraday cup ion collector. One end of the Faraday cup is a grid to allow the air to flow through. The β-source which is in electrical contact with the center manifold stud can be biased either positively, negatively, or maintained at zero potential with respect to the collector. The ion currents are measured with a picoammeter.
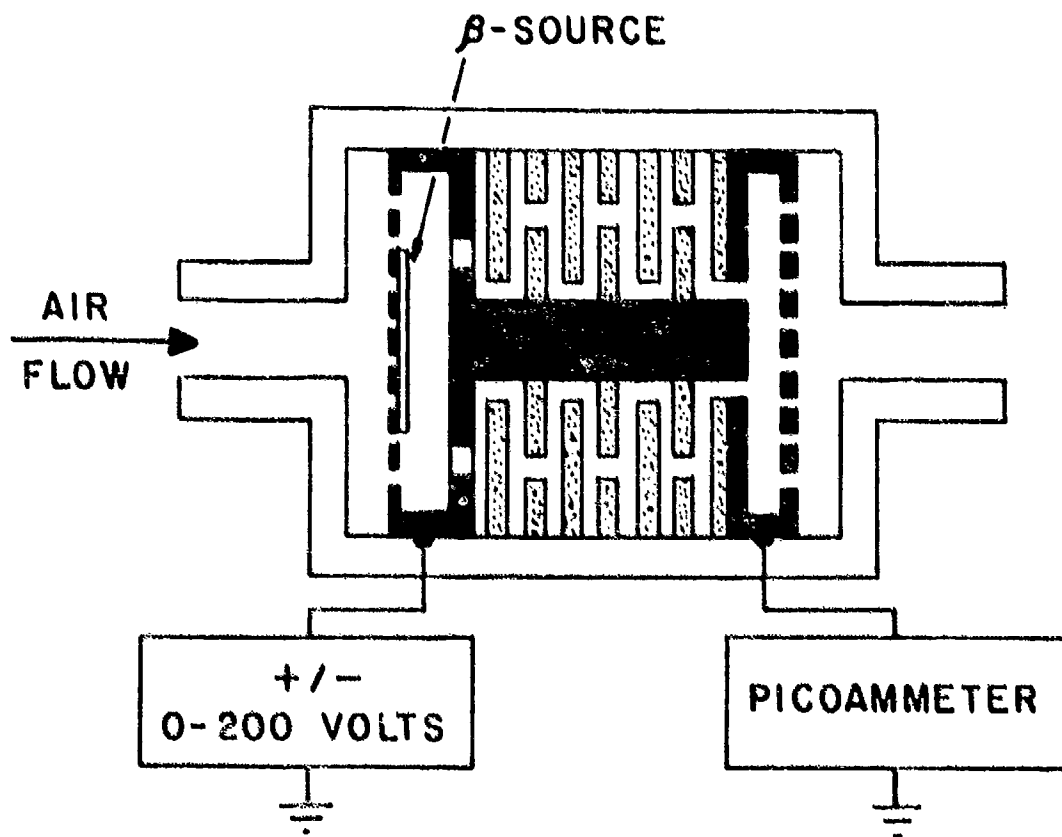

Figure 2. Schematic Diagram of an IDS Cell

Trace concentrations of samples are prepared in a continuous flow system by using air dilution of vapor from the compound of interest.

9

III. RESULTS AND DISCUSSION.

A. Ionic Mass Spectrometry.

Specific ion species indicated in an ionic cluster mass spectrum of dimethyl methylphosphonate are given in the table below.

Identification of DMMP Spectral Elements

Ion	m/e	$I/\Sigma I$ (%)
$H^+(H_2O)_3$	55	2.5
$H^+(H_2O)_4$	73	8.0
$H^+(H_2O)_5$	91	7.0
$H^+(H_2O)_6$	109	1.5
$H^+(DMMP)$	125	11.1
$H^+(H_2O)_7$	127	1.0
$H^+(DMMP)(H_2O)$	143	14.1
$H^+(DMMP)(H_2O)_2$	161	8.5
$H^+(DMMP)_2$	249	43.2
Other	--	3.1

This spectrum was taken using air as the reactant gas at a source pressure of 140 mmHg, [DMMP] = 0.6 ppm, and [H$_2$O] ~ 100 ppm. As can be seen in the table, indicators of the trace compound appear at m/e of [MW + 1 + n(18)], e.g., $H^+(DMMP)(H_2O)_n$, and at m/e of [n(MW) + 1], e.g., $H^+(DMMP)_n$, where n is 1 or 2. A cluster containing a single organic molecule is referred to as a monomer or hydrated monomer if it contains water; those clusters containing two organic molecules are called dimers.

Ions that appear under the category "other" in the table constitute background and can be attributed to clusters formed with methanol and acetone - solvents used in cleaning the apparatus. Consequently, no fragment ions need or can be assigned to the spectral elements.

Figures 3 and 4 illustrate the normalized ion intensities versus pressure of DMMP and dimethyl sulfoxide (DMSO) systems in the pertinent high-pressure regions. Concentrations of DMMP and DMSO are approximately the same (0.6 and 0.7 ppm respectively) and [H$_2$O] ~ 100 ppm. It will be noted that indicators of DMMP appear at lower pressures than those for

DMSO and that the rates of formation of H^+ $(DMSO)_2$ and H^+ (DMSO) are about the same. Without evidence to the contrary, the mechanism of formation of ion clusters for both DMMP and DMSO is assumed to be the same. However, for ion clusters formed from DMMP, the formation of the proton-dimer has predominance over the formation of the proton-monomer, while for DMSO these two reactions have a parity in their probability of occurrence.
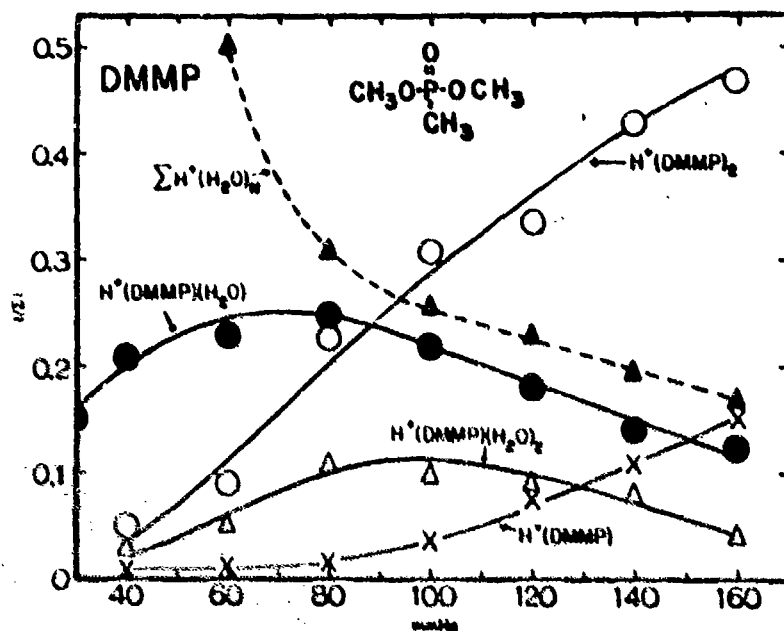

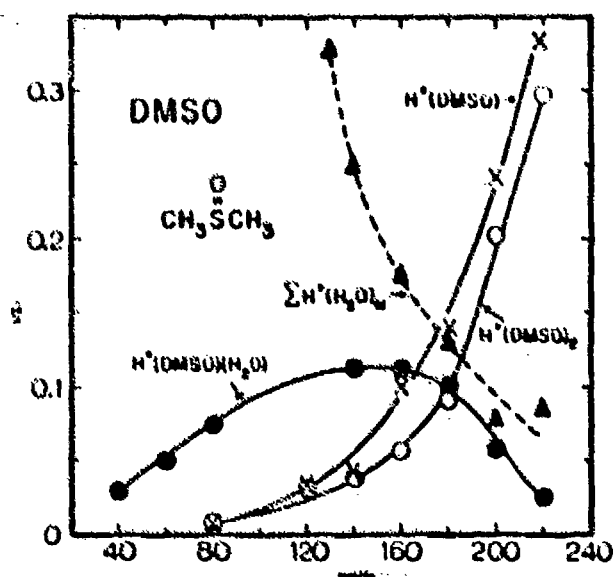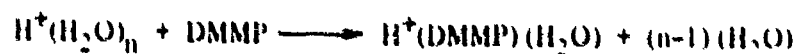Figure 3. Fractional Ion Intensities in DMMP Versus Pressure

Figure 4. Fractional Ion Intensities in DMSO Versus Pressure

11

Dipole moments for DMMP[13] and DMSO[14] are respectively 3.62 and 3.96 Debye units; whereas their polarizabilities, computed from refractive indices, are 10.6 Å^3 and 7.9 Å^3. An explanation for the apparent greater stability and ease of formation of clusters containing DMMP compared to DMSO may be interpreted as a greater influence of polarizability over dipole moment. However, the refractive indices and densities of the two substances are such that the difference in their polarizabilities is primarily a function of their molecular weights. Consequently, while dipole moment and polarizability certainly influence cluster formation, it is assumed that the greater number of vibrational degrees of freedom resident in the DMMP molecule impart a larger stability to its clusters when compared to those of DMSO. This indicates, that within certain unspecified limits, the larger a dipolar molecule the more stable and readily formed will be its ion clusters.

The quantification of the ICMS technique and its sensitivity with respect to trace atmospheric impurities is determined by studying ion cluster formation as a function of the impurity concentration at constant pressure. Figure 5 illustrates the dependence of various ionic cluster concentrations upon DMMP at 140 mmHg. The plotted points indicate experimental data and the smooth curves represent the results of numerically fitting kinetic equations to the data. For the curve-fitting procedure, several reaction mechanisms were considered. The mechanism resulting in the best fit is slightly different from one previously proposed[5] but, nevertheless, is consistent with the qualitative predictions that can be drawn from figures 3 and 4. This mechanism and calculated rate constants are given below.

$$H^+(H_2O)_n + DMMP \longrightarrow H^+(DMMP)(H_2O) + (n-1)(H_2O)$$

$$k = 1.85 \times 10^{-8} \, cm^3 sec^{-1}$$

$$H^+(DMMP)(H_2O) + DMMP \longrightarrow H^+(DMMP)_2 + H_2O$$

$$k = 4.06 \times 10^{-8} \, cm^3 sec^{-1}$$

$$H^+(DMMP)_2 + M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} H^+(DMMP) + DMMP + M$$
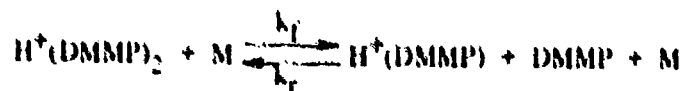
$$k_f = 2.77 \times 10^{-13} \, cm^3 sec^{-1}$$

$$k_r = 7.4 \times 10^{-25} \, cm^3 sec^{-1}$$

The average deviation of the calculated points from experimental data is 12.4%.
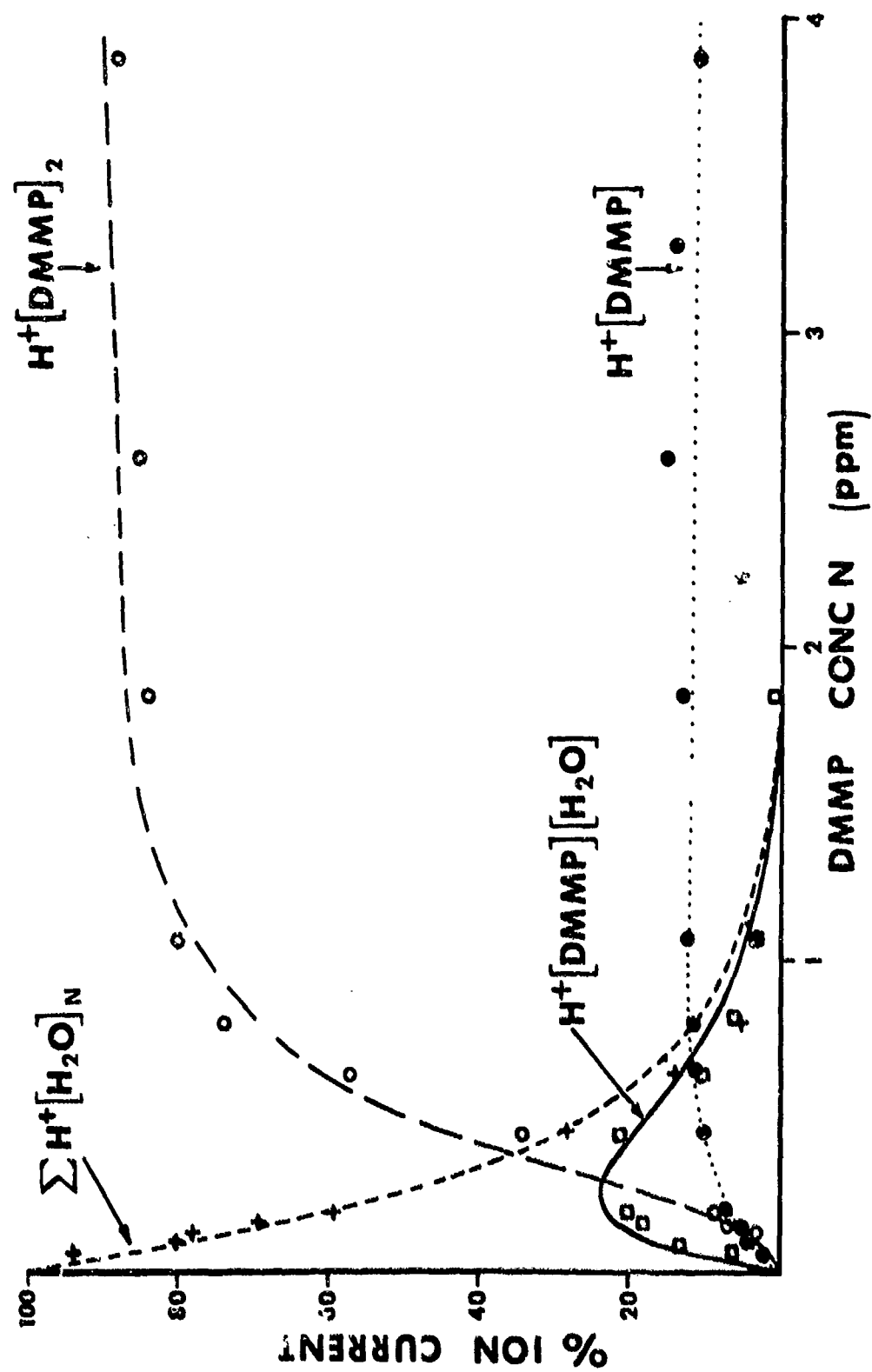
Figure 5. ICMS Relative Ion Intensities Versus [DMMP]

At concentrations near the threshold sensitivity the indicators of the trace impurities are $H^+(A)(H_2O)$, where A is an impurity molecule. At higher concentrations, a few ppm, the ionic cluster mass spectrum consists only of the ionic clusters $H^+(A)_n$, where n is usually 1 and 2. The best sensitivity that has been observed, to date, is 0.5 ppb of diisopropyl methylphosphonate (DIMP).

B.   Ionization Detector System.

It is now well understood that the charge carriers in ionized air, at or near atmospheric pressure, are in the form of ionic clusters, regardless of the source of primary ionization. It is, therefore, evident that responses in the IDS are caused by changes in densities of ionic clusters as a function of trace impurity concentration as air flows through the detection cell (figure 2). The current changes usually appear as increases (increase in positive ion cluster concentration) when an impurity is introduced into a clean moist airstream.

Both positive and negative primary ions are formed in the β-source region of the detector cell and react with neutral molecules to form positively and negatively charged clusters. In the absence of atmospheric impurities the positive clusters are $H^+(H_2O)_n$ and the negative clusters are primarily $O_2^-(H_2O)_n$.[15] Under these conditions, more positive clusters than negative clusters reach the collector per unit time. The net result is a positive current measured at the collector.

When impurities are present in the air, reactions between the impurity molecules and the hydrate clusters result in the replacement of water in the clusters by the impurity. The clusters thus produced are larger in size and, presumably, more stable.

1.   Qualitative Response Studies.

At the beginning of a series of parametric studies on the IDS, qualitative "sniff" tests were run for approximately 60 compounds. In general, the IDS responses were positive, i.e., there were increases in the net positive cluster concentrations at the collector. Some compounds showed an increase in the net negative ion current (examples are most chloro compounds) and some showed no change in cell current.

Examination of the responses of an homologous series of primary alcohols (methyl through n-butyl) showed that the larger the impurity molecule, the larger the cell response. It was also noted that large concentrations of ammonia caused no cell response. Ammonia is known to react very well to form ammonia-water ion clusters[11] and the cluster size distribution is essentially the same as that with only water present. The conclusions drawn from these observations are (a) the larger molecules form larger clusters and (b) since larger clusters have small diffusion velocities normal to the flow streamlines they have a greater probability of surviving the flow region and increasing the collector current.

The conclusions derived from the qualitative observations were tested by measuring the response of the IDS to quantitative mixtures of several homologous series of impurity compounds.

Primary alcohols (methanol through n-pentanol) were studied at concentrations of 25 and 50 ppm. At each concentration the order of response was n-pentanol > n-butanol > n-propanol > ethanol > methanol. An ICMS analysis of methanol, ethanol, and n-propanol, each at a concentration of 25 ppm in air, shows that the alcohols readily react to form ionic clusters $H^+(ROH)_n(H_2O)_m$ and that the average mass of the clusters increases with increasing molecular weight.

A series of CW agent simulants (phosphonate esters) was studied as functions of concentration and flow rate. The series consisted of diisopropyl methylphosphonate (MW 180), diethyl ethylphosphonate (MW 166), dimethyl methylphosphonate (MW 124), and dimethyl hydrogenphosphonate (MW 110). The results for DIMP and DMMP are shown in figure 6. The other members of the series were left out for the sake of clarity. As can be seen, the response increases to saturation with concentration. At any given concentration and flow rate the response due to DIMP > DEEP > DMMP > DMHP.
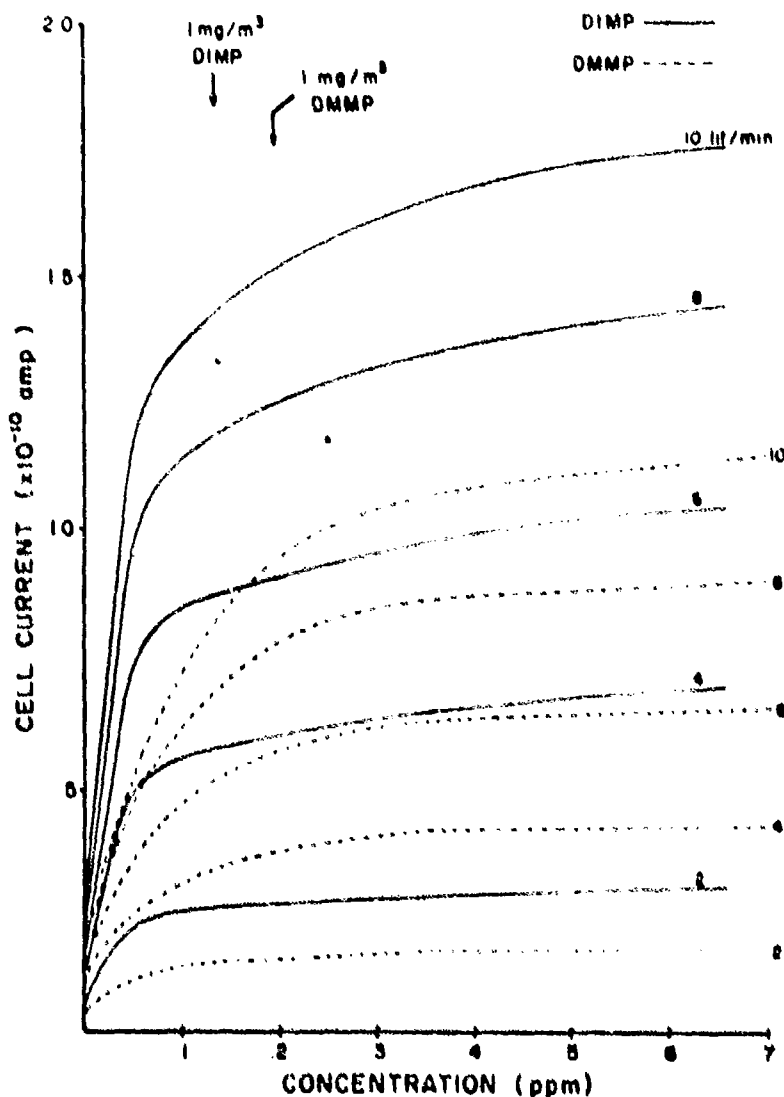

Figure 6. IPS Response Versus Concentration at Several Flow Rates

Three amines were tested quantitatively and the same behavior was noted; namely, the response of diisopropyl amine > diethyl amine >> ammonia.

The IDS response shows different response characteristics to acids. At low concentrations the response decreases (increases negatively) markedly. As concentration is increased further the response passes through a minimum and then increases toward saturation. The negative ion clusters are formed faster at lower concentrations and tend toward saturation sooner than the positive ions. The magnitude of responses (both positive and negative) due to the acids studied is butyric acid > acetic acid.

All of the quantitative work done so far shows that, within a homologous series, the larger molecules result in larger ion clusters and procedure greater IDS responses. Thus, the quantitative studies seem to verify that the size of the ionic clusters, therefore, diffusion, plays a predominant role in the IDS response mechanism.

2.   Diffusion Studies.

The effect of cluster size can be demonstrated by studying the IDS response to water vapor at various airflow rates. The positive I^+, negative I^-, ion currents (+ and - 200 volts source bias) were measured as a function of flow rate, Q, up to about 8.5 ℓ/min. The relationship between I and Q was empirically found to be

$$I = K \cdot Q^{3/2}$$

In the vicinity of the source of ionization the concentrations of positive and negative ions is dependent upon temperature, pressure, and β-source activity. These parameters are held constant so that the ion density in the ion source region is constant. The ion loss mechanism in this region of the detector is primarily recombination which reduces both positive and negative ion concentrations by the same amount.

To a first approximation the cell geometry is considered as a straight cylindrical tube of volume V (the effective internal volume of the baffle section of the cell) and radius r (half the average spacing of the various components of the baffle section). A certain number of ions per unit area, N_0 is introduced into the baffle section. Only radial diffusion is considered since axial diffusion does not result in a loss of ions. The one dimensional diffusion equation with the approximation for small distance is

$$n(x, t) = \frac{N_0}{2\sqrt{\pi D t}} \exp\left[-\frac{x_2}{4 D t}\right] \approx \frac{N_0}{2\sqrt{\pi D t}}$$

where

   $n(x,t)$ = the ion concentration at a radial distance x from the tube axis at time t after the initial introduction of ions;

   D = the diffusion coefficient.

An ion is considered to be lost and therefore not able to reach the ion collector when it has diffused through the distance, r (the radius of the approximating tube). The ion concentration at the collector end of the tube is then given by

$$n(t) = \frac{N_0}{2\sqrt{\pi D t}}$$

Integration of the above along the radial distance of diffusion provides the number of ions per unit area at the collector.

$$\int_0^r n(t)dx = N(t) = \int_0^r \frac{N_0 dx}{2\sqrt{\pi D t}} = \frac{N_0 r}{2\sqrt{\pi D t}}$$

The equality of ratios for ions per unit area, N, and ion concentration, n, can be made

$$\frac{N(t)}{N_0} = \frac{n(t)}{n_0} = \frac{r}{2\sqrt{\pi D t}}$$

Therefore,

$$n(t) = \frac{n_0 r}{2\sqrt{\pi D t}}$$

The ion current at the collector is

$$I = n(t) q Q$$

where

$$q = \text{the electronic charge } (1.6 \times 10^{-19} \text{ colomb}).$$

Therefore,

$$I = \frac{n_0 r q Q}{2\sqrt{\pi D t}}$$

17

the time, t, is the residence time of particles in the tube and is V/Q. Substituting for t, the positive or negative ion current at the collector is

$$I = \frac{n_o \, r \, q \, Q^{3/2}}{2\sqrt{\pi D V}}$$

Thus, the average ionic diffusivity can be determined from the slope, K of a plot of I versus $Q^{3/2}$. In a typical IDS cell, $r = 0.038$ cm and $V = 0.19$ cm^3. Dimensions of the ion source region are such that recombination of positive and negative ions is an efficient mechanism for ion loss when ion concentrations are greater than 1.5×10^7 ion/cm^3; below this concentration recombination is unimportant. Therefore, the value chosen for n_o is 1.5×10^7 ions/cm^3 for both positive and negative ions.

Then,

$$D = \left[\frac{n_o \, r \, q}{2K}\right]^2 \cdot \frac{1}{\pi V} = \frac{1.61 \cdot 10^{-23}}{K^2}$$

where

I is measured in amperes and Q in ℓ/min.

Figure 7 represents the results of diffusion studies (I versus $Q^{3/2}$) for moist air. At low humidity, separate and distinct curves are obtained for positive and negative ions. This indicates that the negative ions are smaller than the positive ions. When the humidity is increased, ionic diffusivity decreases (larger ions are formed), and the curves coincide; oppositely charged ions are essentially the same size. The values of diffusivities calculated from these data agree very well, considering the complexity of the acutal cell geometry, with typical ion diffusivities (0.06 cm^2/sec) reported in the literature,[16] and are summarized below.

Relative humidity (25°C)	D^+ (cm^2/sec)	D^- (cm^2/sec)
15%	0.075	0.094
63%	0.052	0.052
92%	0.030	0.030

The observed decrease in D with humidity is consistent with the well-known fact that the average size of hydrated-ion clusters increases with $[H_2O]$.
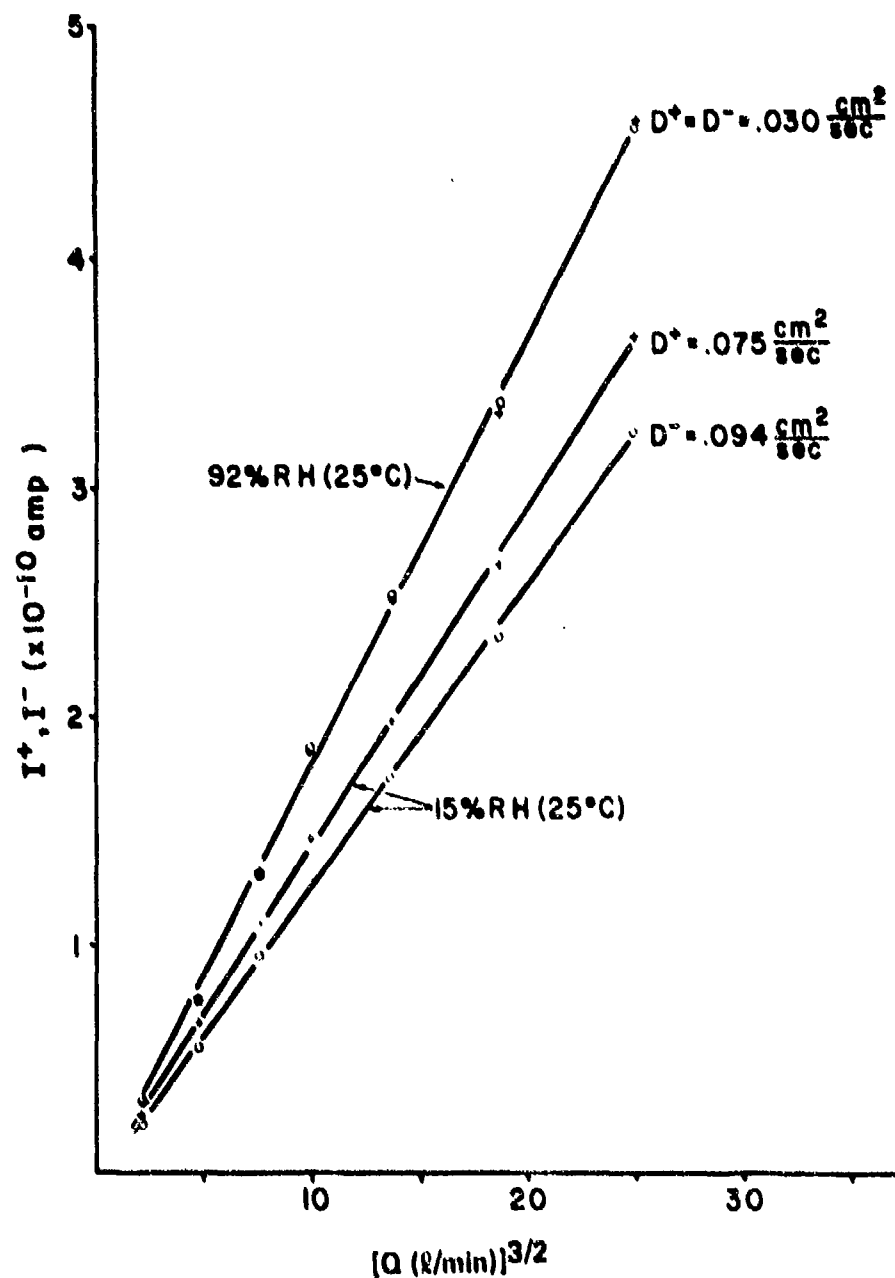
Figure 7. Positive and Negative IDS Response As
a Function of Flow Rate

The conclusions drawn from these studies is that differential diffusion of ionic clusters from an airstream predominates in the phisics of the response mechanism. An independent study of the IDS mechanism* has substantiated the conclusions of this work with respect to the diffusion mechanism.

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*McClure, B. T., and Waletzko, J. A. Ionization Detector System (IDS) Mechanism. Unpublished work. Honeywell, Inc., Minneapolis, Minnesota.

IV. SUMMARY.

A. Ionic Cluster Mass Spectrometry.

Irrespective of the subtle aspects associated with ion cluster stability, the fact remains that the techniques producing them offers an opportunity for application to the detection and analysis of trace compounds in the gas phase. The ability to use atmospheric gases as reactants considerably extends the practical applicability of this technique. Its incorporation with gas chromatographic analysis of trace compounds (where N_2 is a common carrier gas) has many possibilities. Several features that enhance its general attractiveness are: (1) the absence of a spectrum complicated with fragment ions, (2) high mass peaks directly related to the molecular weight of the compounds, and (3) sensitivity well below the ppm concentration range.

B. Ionization Detector System.

It has been shown that the charge carriers in the IDS are ionic clusters of water and trace gas molecules. The ability to use such a system as a detector of trace atmospheric impurities is obtained from the facts that: (1) ion clusters are readily formed in moist air, (2) the presence of trace impurities tends to form larger, more stable clusters, rapidly, and (3) the smaller diffusivities of the large ionic clusters provide a means of separating the clusters according to size.

Although the IDS responds (with varying sensitivity) to many compounds it is essentially nonresponsive to "normal" atmospheric pollutants (e.g., NO_x, SO_2, H_2S, etc.) and other compounds of low molecular weight. Therefore, interferences from these substances and others likely to be found in a realistic environment of its intended use are minimal. Whatever inadequacies such a system suffers in its lack of specificity for detection are made up in its inherent sensitivity and its simplicity.

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24

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